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(71) Applicant *(for all designated States except US)*: IMPERIAL COLLEGE OF SCIENCE, TECHNOLOGY AND MEDICINE [GB/GB]; Sherfield Building, Exhibition Road, London SW7 2AZ (GB).

(72) Inventors; and
(75) Inventors/Applicants *(for US only)*: CHOY, Kwang-Leong [MY/GB]; 35 Blondvil Street, Cheylesmeore, Coventry CB3 5EQ (GB). CHANG, Isaac, Tsz, Hong [GB/GB]; School of Metallurgy and Materials, University of Birmingham, Edgbaston, Brimingham B15 2TT (GB).

(74) Agent: TURNER, James, Arthur; D. Young & Co., 21 New Fetter Lane, London EC4A 1DA (GB).

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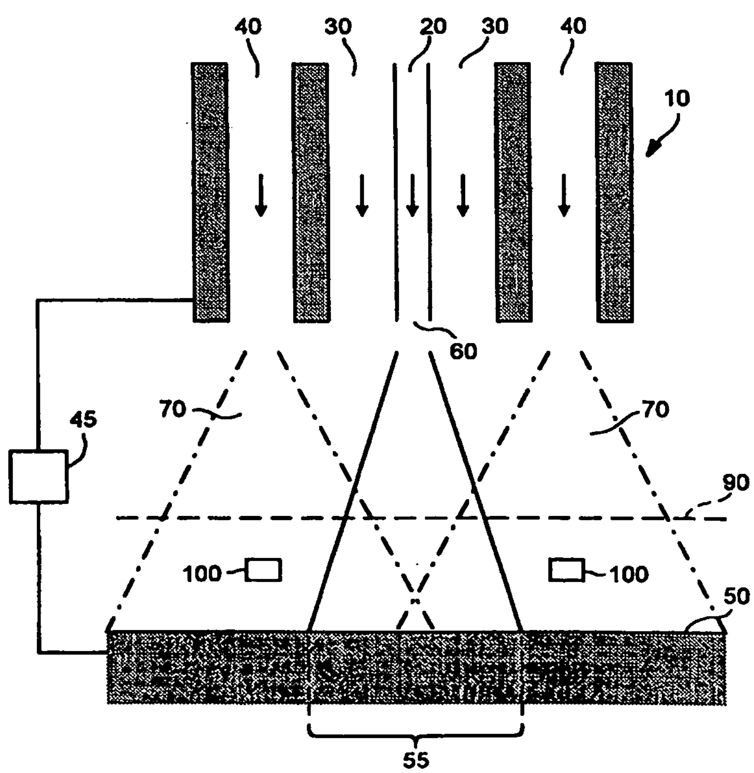
(54) Title: MATERIAL DEPOSITION

(57) Abstract

A method of depositing a material on a substrate comprises the steps of: (a) passing a precursor liquid through an outlet to generate a stream of droplets of the precursor liquid directed towards the substrate; (b) applying an electric field between the outlet and the substrate; and (c) generating a flame between the outlet and the substrate so that the stream of droplets of the precursor liquid from the outlet pass through the flame before reaching the substrate.



MATERIAL DEPOSITION

This invention relates to material deposition, for example as a film or layer on a substrate, or as a powder.

The applications of materials such as ceramics as structural coatings and functional electronic films are expanding rapidly. Various deposition techniques such as chemical vapour deposition (CVD), physical vapour deposition (PVD), flame spraying deposition (FSD), combustion chemical vapour deposition (CCVD) and sol-gel deposition have been developed or investigated.

Both CVD and PVD involve the use of sophisticated and expensive deposition chambers and/or vacuum systems. Applications of CVD and PVD methods to ceramic films are limited to coating processes in which the available film thickness and coating areas are relatively small.

It is often difficult to control the stoichiometry of multicomponent oxide films with CVD, and problems can also arise due to differences in vapour pressure of the CVD reagents and the low growth rate of the CVD films.

PVD methods such as radio frequency (RF) sputtering tend to give low deposition rates and poor yields. Reactive magnetic sputtering and ion beam sputtering need expensive equipment and skilled operators.

Flame synthesis deposition produces films with morphology, microstructure and electrical properties dependent on the temperature of the substrate, the coating concentration, the carrier gas flow rate and so on. Control of all of these variables to achieve a desired coating is difficult.

This invention addresses these problems by providing a deposition technique which at least alleviates some of the disadvantages of the prior art.

This invention provides a method (and a corresponding apparatus) for depositing a material on a substrate, the method comprising the steps of:

(a) passing a precursor liquid through an outlet to generate a stream of droplets of the precursor liquid directed towards the substrate;

(b) applying an electric field between the outlet and the substrate; and

(c) generating a flame between the outlet and the substrate so that at least a portion of the stream of droplets of the precursor liquid from the

outlet pass through the flame before reaching the substrate.

The invention provides a new technique which, in at least preferred embodiments, involves spraying atomised precursor droplets into a flame while providing an electric field between the precursor outlet and the substrate, so that the precursor forms a charged aerosol which undergoes combustion and/or chemical reactions in the vapour phase in the vicinity of the substrate This can result in the formation of a stable solid film with good adhesion onto the substrate.

The invention will now be described, by way of example only, with reference to the accompanying drawings, throughout which like parts are described by like references and in which Figure 1 is a schematic diagram of a deposition apparatus.

Figure 1 schematically illustrates a deposition apparatus comprising a coaxial nozzle assembly 10 having a liquid precursor delivery capillary 20, a first coaxial passage 30 for cold air, nitrogen or other gases, and a second coaxial passage 40 for liquid or gaseous fuel.

The precursor can be, for example, one of the precursors listed in WO97/21848, with or without the catalyst described in that document. Many other precursors can be used as appropriate for the desired deposition, such as precursors known from the field of flame synthesis deposition (see publication reference 1).

The fuel may be a mixture of oxygen and acetylene, or another appropriate fuel such as fuels known from the field of flame synthesis deposition.

A high voltage source 45 maintains an electric field between the nozzle assembly 10 and a substrate 50. The potential difference between these two parts may be, for example, within the approximate ranges described in WO97/21848, such as in the approximate range of 5 - 30 kV.

The precursor liquid is sprayed towards a region 55 of the substrate 50 from an outlet 60 of the capillary 20. The fuel is ignited so that an annular combustion region 70 is generated. The extent of this combustion region can be controlled by controlling the fuel flow rate, the distance between the nozzle assembly 10 and the substrate 50, the amount and flow rate of cold gases in the passage 30, and the applied electric field.

Decomposition and/or chemical reaction of the precursor (e.g. a sol to gel transition) occurs in a higher temperature region of overlap between the spray of

precursor from the outlet 60 and the combustion region 70. Deposition occurs in or beneath this overlap zone. So, by controlling the extent of the combustion region as described above, the deposition on the substrate can be controlled, and premature reaction or decomposition can be avoided (a problem in many prior art flame deposition techniques, leading to non-uniform deposition).

Either polarity of electric field can be used, or a periodically or occasionally alternating field can be employed. A thermocouple can be used to monitor the temperature of the substrate.

An optional mesh 90 helps to remove soot from the flame and so help to provide a high temperature (blue) flame.

A further optional annular electrode connectable to the high voltage supply 45 at an intermediate potential between that of the nozzle and that of the substrate can be used to steer the deposition onto a required area.

The technique is also applicable to premixed fuel and precursor systems. However, non premixed systems are preferred as this gives greater control of the deposition temperature and helps to avoid premature decomposition.

The technique can be used to manufacture metal oxide and non-oxide materials; to fabricate pure, doped, multicomponent or multiphase materials; to manufacture materials with dense, porous or a combination of dense and porous structures; to manufacture composite, multilayer and compositionally graded structures; to produce thin or thick films; for rapid prototyping of net shape and near net shape components; or to coat planar or tubular substrates or other complex shaped components. The process can be scaled up for large area or mass production. This can be achieved using multiple flame / electrostatic units. For accurate deposition and process control, the process can be automated.

Conductive or non-conductive substrates can be used. For non-conductive substrates, the conductivity can be improved by having a conductive backing holder.

The process can be performed in an open atmosphere or in an inert / controlled atmosphere. For example, oxide-based structures can be deposited in an open atmosphere, or non oxides such as sulphides, carbides etc can be produced in a controlled atmosphere. Deposition can take place at atmospheric or a different pressure.

The chemistry of the precursor(s) can be adjusted so that once the chemical reaction starts to take place, a self-assisted reaction occurs. This can reduce the requirements for fuel while still achieving the required deposition temperature for a particular material.

The electric field helps to reduce the loss of precursor to the surroundings by directing the precursor to the deposition surface, a clear advantage over conventional flame-based techniques.

The deposition can be controlled by one or more of the following: the flow rate of the cold gas; the electric field strength; the fuel and its flow rate; the separation of the nozzle assembly from the substrate; the chemistry, concentration and flow rate of the precursor; and the deposition pressure.

Embodiments of the invention allow the use of simple, flexible and/or mobile equipment. The process can be relatively safe by the use of sol precursors and/or water based precursors. The process can give rise to an advantageously low flame / deposition temperature for crystalline materials (e.g. 550-800°C for Y_2O_3-ZrO_2). Dense films tend to require a sol precursor, whereas porous films may be based on sol or water based precursors. The consumption of precursor can be relatively low, e.g. 1 ml of 0.05M solution to generate a 1 micron film measuring 1cm x 1cm. The process can be a single step without the need for a subsequent heat treatment.

Powders can be formed by allowing the precursor's chemical reaction to solid to take place above the substrate. The substrate is then deposited with discrete powder particles which can be collected later from the substrate surface. Powder generation can be improved by employing gas condensation techniques and a cooled collecting substrate.

In a further embodiment, the substrate can be mounted on a moveable table or XY positioner (not shown) under the control of, for example a computer aided design (CAD) system (not shown) to allow a three dimensional object to be constructed layer by layer. This can be used in, for example, rapid prototyping systems.

PUBLICATION REFERENCES

1. Choy, K L, "Flame Assisted Vapour Deposition of Ceramic Films and Coatings", British Ceramic Proceedings, The Institute of Materials (1995), pp65-74

2. Hunt, A T et al, Applied Physics 63 (1993) No 2, pp266-268

The following patent documents are also mentioned as background art: WO97/21848, GB-A-2 192 901, GB-A-2 162 861, EP-A-0 103 505, US-A-5 652 021, US-A-5 534 311 and SE-A-9504410.

CLAIMS

1. A method of depositing a material on a substrate, the method comprising the steps of:
   (a) passing a precursor liquid through an outlet to generate a stream of droplets of the precursor liquid directed towards the substrate;
   (b) applying an electric field between the outlet and the substrate; and
   (c) generating a flame between the outlet and the substrate so that at least a portion of the stream of droplets of the precursor liquid from the outlet pass through the flame before reaching the substrate.

2. A method according to claim 1 wherein the material is a ceramic material.

3. A method according to claim 1 or claim 2 wherein the material is a multicomponent oxide material.

4. A method according to any one of the preceding claims, comprising the step of:
   (d) heating the substrate.

5. A method according to any one of the preceding claims, in which the precursor liquid is a sol precursor solution.

6. A method according to any one of the preceding claims, comprising the step of moving the substrate and/or the outlet during deposition so that a three-dimensional structure is deposited as a series of overlying deposited layers.

7. A method according to any one of the preceding claims, comprising controlling a region of deposition by varying one or more of the rate of flow of fuel to provide the flame, the separation between the outlet and the substrate and the electric field between the outlet and the substrate.

8. A method according to any one of the preceding claims, comprising the step of providing a flow of cold gas in a direction from the outlet towards the substrate.

9. Apparatus for depositing a material on a substrate, the apparatus comprising:

(a) an outlet;

(b) a precursor supply operable to pass a precursor liquid through the outlet to generate a stream of droplets of the precursor liquid directed towards the substrate;

(c) an electrical supply for applying an electric field between the outlet and the substrate; and

(d) a burner for generating a flame between the outlet and the substrate so that at least a portion of the stream of droplets of the precursor liquid from the outlet pass through the flame before reaching the substrate.

10. Apparatus according to claim 9, comprising a coaxial outlet assembly having a plurality of coaxial outlets, one of the coaxial outlets carrying the precursor liquid and another of the coaxial outlets carrying fuel to provide the flame.

11. Apparatus according to claim 10, in which another coaxial outlet is arranged to carry a flow of cold gas.

12. Apparatus according to claim 10 or claim 11, in which the precursor liquid is carried by a central outlet of the coaxial outlet assembly.

13. Apparatus according to any one of claims 9 to 12, comprising a mesh disposed between the precursor liquid outlet and the substrate.

14. Apparatus according to any one of claims 9 to 13, comprising an electrode at an electric potential between the potential of the precursor outlet and the potential of the substrate and disposed between the precursor outlet and the substrate.

15. Apparatus according to claim 14, in which the electrode is an annular

electrode.

16. Apparatus according to any one of claims 9 to 15, comprising a positioner for altering the relative position of the precursor outlet and the substrate.

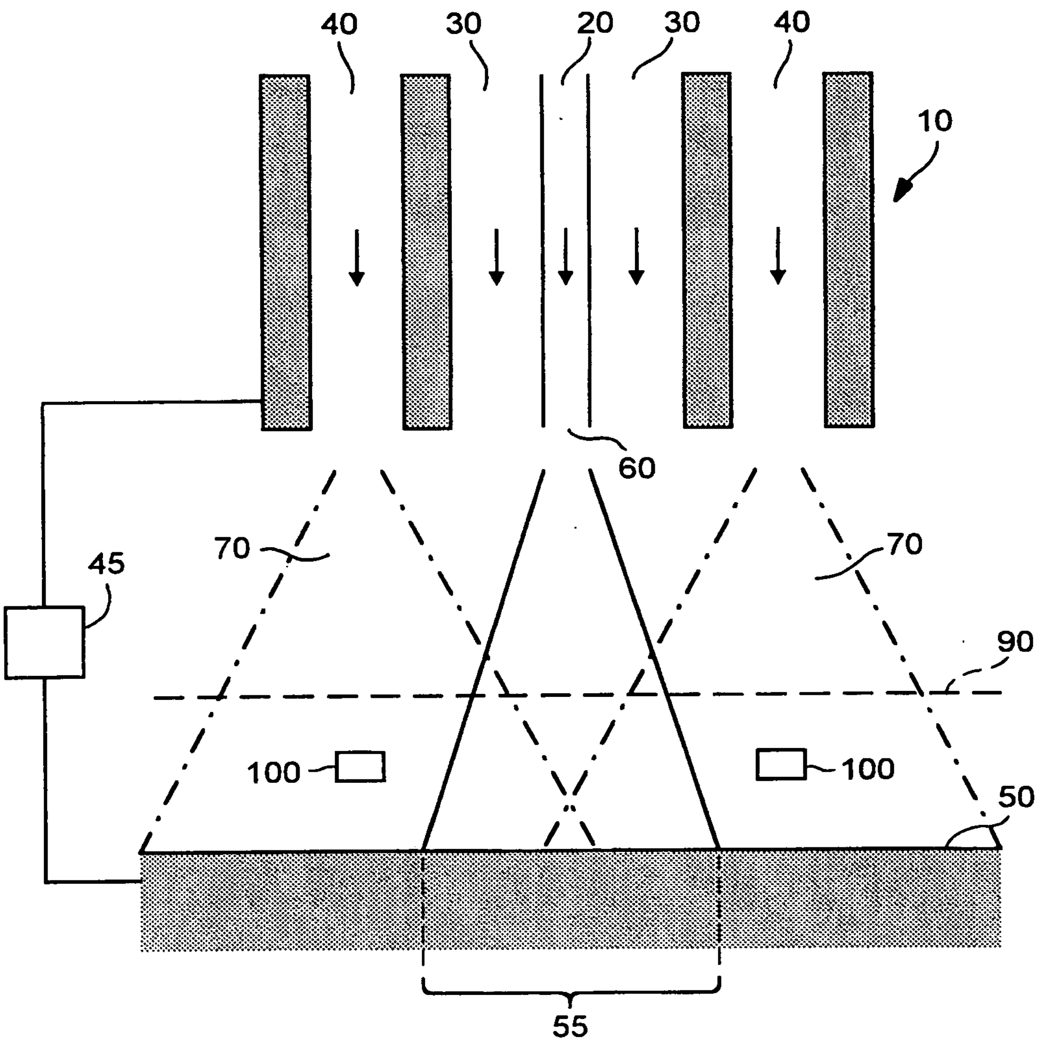


FIG. 1